To: technicalreports@afosr.af.mil

Subject: Final Statement to Dr. Donald Silversmith

Contract/Grant Title: Development and Investigation of Bismuth

Nanowires – Start up phase

Contract/Grant #: **FA9550-07-1-0472** 

Reporting Period: June 1, 2007 to May 31, 2008

Annual accomplishments (200 words max): The project aims to develop Bimuth and Bimuth-based nanowires and explore their application in sensing and uncooled IR detection. It has made significant progress in this seedling phase. Two methods for synthesizing Bi and BiS nanowires have been developed as a result. One method offers the advantage of having both uniform and pre-defined diameters in the fabricated Bi nanowire array. It is developed from a template-based growth technique that was first demonstrated by our group a decade earlier and has now been further improved with controllable diameter variation. The second method makes use of a redox biomolecule, glutathione, a well known antioxidant abundant in fruits, as both a feedstock and self-assembling agent. The biosynthesized BiS nanowires are remarkable in that they have a high degree of structure uniformity and an expected highest thermoelectric powers that will be proven in the follow-on phase.

Archival publications (published) during reporting period:

1. Two manuscripts are being prepared for submission to refereed journals.

Changes in research objectives, if any: None

Change in AFOSR program manager, if any: None Extensions granted or milestones slipped, if any: None Include any new discoveries, inventions, or patent disclosures during this reporting period (if none, report none): None

### **REPORT DOCUMENTATION PAGE**

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# Final Report

Development and Investigation of Bismuth Nanowires - Start up phase

FA9550-07-1-0472

To Dr. Donald Silversmith

AFOSR

PI: Jimmy Xu
Brown University
184 Hope St., Providence, RI 02912

**Objectives:** In the start-up phase of an exploratory research, to develop a new generation of nano-electronic structures made of Bismuth, that is semimetal in its bulk form but can function as a semiconductor in the form of one-dimensional nanowires, with a semiconductor bandgap being tunable (inversely) with the wire diameter,

Status of Effort: We have completed the start-up phase of the project by meeting and exceeding the stated goal of proving the feasibility of bismuth-based nanowire fabrication. Specifically, we have shown that uniform Bi nanowires can be grown inside the nanopores of a template by electrodeposition and BiS nanowires can be synthesized using a redox biomolecule. Building up from the understanding developed in this start-up phase, we plan to pursue a more ambitious research plan, if more funds could be secured, to develop this new nanowire system into a platform for uncooled IR detections with a variable spectral range.

## **Accomplishments/New Findings:**

We have developed two methods for synthesizing Bi and BiS nanowires. One method offers the advantage of having both uniform and pre-defined diameters. It is developed from a template-based growth technique that was first demonstrated by our group a decade earlier and is now furthered with controllable diameter variation. It begins with the formation of a growth template which is accomplished by anodization of high purity aluminum. Under a set of optimized conditions, nanopores will form and self-organize into a highly ordered array of straight nanopores in the Anodized Aluminum Oxide (AAO) to serve as the growth template. With the use of the template, uniform Bi nanowires can be grown inside the nanopores by electrodeposition. We found that by superimposing an AC field on the conventional electrodeposition process that is normally under a DC field, we could obtain nanowires with uniform diameter along the length. The



Figure 1. SEM and TEM images of Bi nanowires

nanowires grown within the template can be freed out of the template by dissolving the AAO matrix as shown in Fig. 1.

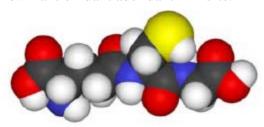
The nanowire diameter can be controllably changed by changing the anodization voltage.

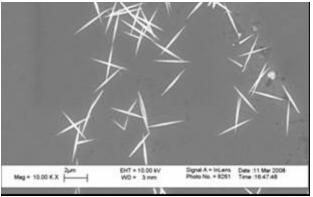
After freeing out the grown homo-junction nanowires by dissolving away the template, we can assemble the Bi nanowires onto external metal electrodes by either the ensemble electrophoresis technique or the more precise DNA-hybridization controlled assembling of individual nanowires (*APL*, 1999). In the next phase, we will conduct experiments on the two-terminal diode configuration, and test their device functionalities and, in particular, the expected high IR photovoltaic responses in the un-cooled mode of

operation as well as in the reverse operation mode for high-efficiency thermoelectric figure of merit (ZT).

Our effort in developing a second method for synthesizing Bi-based nanowires has also met with success. BiS nanowires with a high degree of structure uniformity have been obtained for the first time, as shown figure 2 below.

This second method makes use of a redox biomolecule, glutathione, a well known antioxidant abundant in fruits.





The exact chemical reaction process and the nanowire formation mechanism are yet to be understood in the next phase of the exploration. Judging from the great uniformity of the resultant nanowire structures, we hypothesize that the redox nature of the glutathione provides a S ion with each molecule which coordinates the adsorption and then reaction with Bi ions. In the next phase, we will seek for a clear understanding of the mechanism and process of the glutathione enabled formation of BiS nanowires.

<u>Personnel Supported:</u> Hongsik Park (Ph.D graduate student), Jin Ho Kim (Postdoctoral Associate), and Jimmy Xu (PI).

**Publications:** Two papers are in preparation for submission in refereed journals.

<u>Interactions/Transitions:</u> Magnolia Optical Technologies Ltd. Woburn, MA. (Dr. A.K Sood); Kookmin University, Korea (Professor Shin).

New Discoveries: None

**Honors/Awards:** None